# WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



(51) International Patent Classification 5:		(11) International Publication Number: WO 93/19148
C11D 1/722, 1/83	A1	(43) International Publication Date: 30 September 1993 (30.09.93
(21) International Application Number: PCT/US (22) International Filing Date: 15 March 1993		Company, 5299 Spring Grove Avenue, Cincinnati, OF
(30) Priority data: 92870045.9 17 March 1992 (17.03.92) (34) Countries for which the regional or international application was filed:	) BE et	(81) Designated States: AU, BB, BG, BR, CA, CZ, FI, HU, JP KP, KR, LK, MG, MN, MW, NO, NZ, PL, RO, RU SD, SK, UA, US, European patent (AT, BE, CH, DE DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE) OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML MR, SN, TD, TG).
(71) Applicant (for all designated States except US): TH TER & GAMBLE COMPANY [US/US]; One Gamble Plaza, Cincinnati, OH 45202 (US).		
(72) Inventors; and (75) Inventors/Applicants (for US only): DE WAELL Karel, Emma [BE/BE]; Meerweg 33, B-1980 Ze SCOTT, Louise, Gail [GB/BE]; Stijn Streuvelsl 1933 Sterrebeek (BE).	mst (B	3).

(54) Title: COMPOSITIONS AND METHOD FOR DILUTE CLEANING OF HARD SURFACES

## (57) Abstract

The present invention encompasses hard surface cleaning compositions comprising highly ethoxylated nonionic surfactants, possibly in mixture with anionic surfactants. The present invention also encompasses a method of cleaning a hard surface wherein said compositions are diluted in water and applied to said hard surface. The present invention also encompasses the diluted cleaning composition obtained in the method according to the present invention.

## FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

agtingreen a

THE STATE

• •
ion
;
Merica
5 M 1
Astrat .

COMPOSITIONS AND METHOD FOR DILUTE CLEANING OF HARD SURFACES

## Technical field

The present invention relates to the cleaning of hard surfaces. Hard surface cleaning compositions comprising a at least one one highly ethoxylated nonionic surfactant and possibly an anionic surfactant, are diluted before use, exhibiting outstanding dilute cleaning performance.

### Background

Hard surface cleaning compositions are well known in the art. It is known to use various surfactants in these compositions, including ethoxylated nonionic surfactants. Ethoxylated nonionic surfactants which are typically used in such compositions are lower ethoxylates, i.e. with a degree of ethoxylation of 5 to 7.

Compositions which can be used in diluted form are also known in the art. In such compositions, the technical problem lies in sustaining upon dilution an efficient cleaning performance. Such compositions for dilute cleaning are described for instance in copending European Patent Application EP 91870109.5. In these compositions, the dilute cleaning performance is obtained by using alkanolamines.

2

It is thus an object of the present invention to provide hard surface cleaning compositions which can be effectively used in diluted form.

It has now been found that this object could be met by formulating hard surface cleaning compositions comprising at least one highly ethoxylated nonionic surfactant, preferably with at least one anionic surfactant. These compositions unexpectedly exhibit outstanding cleaning performance upon dilution, compared to the same compositions without said nonionic surfactant while the cleaning performance of the neat, i.e. undiluted compositions is similar, regardless of the presence of said nonionic surfactant.

In other words, it has now been found that hard surface cleaning compositions comprising said highly ethoxylated nonionic surfactant exhibit outstanding cleaning performance when used both neat and diluted.

Surprisingly, said compositions comprise a highly ethoxylated nonionic surfactant, yet they are especially effective on greasy soils. Such greasy soils are commonly brought by cooking with oils and fatty foods, and by simple contact with human skin, thus they are present on most surfaces, particularly in bathrooms and kitchens. The compositions according to the present invention are suitable for use on all such surfaces.

This invention is also particularly useful as it allows to formulate compositions with reduced levels of other ingredients, which yet retain optimal cleaning performance, due to said highly ethoxylated nonionic surfactant; also, the user needs less product to achieve the same task. This advantage is particularly valuable in terms of environmental compatibility.

Compositions comprising highly ethoxylated fatty alcohols are described in SU 595369 (abstract). These compositions are designed for the cleaning of metallic surfaces in weaving machines.

#### Summary of the invention

The present invention thus encompasses a composition for the cleaning of hard surfaces comprising from 0.5 % to 30 % by weight of the total composition of at least one nonionic surfactant, characterized in that said nonionic surfactant is of the formula  $RO-(CH_2CH_2O)_nH$  wherein R is a  $C_8$  to  $C_{22}$  alkyl chain or a  $C_8$  to  $C_{28}$  alkyl benzene chain, and n is an integer of from 21 to 65, or mixtures thereof.

The present invention also encompasses a composition for the cleaning of hard surfaces comprising from 0.5 % to 30 % by weight of the total composition of a mixture comprising at least one anionic surfactant and at least one nonionic surfactant, characterized in that said nonionic surfactant is of the formula  $RO-(CH_2CH_2O)_nH$  wherein R is a  $C_8$  to  $C_{22}$  alkyl chain or a  $C_8$  to  $C_{28}$  alkyl benzene chain, and n is an integer of from 10 to 65, or mixtures thereof.

The present invention also encompasses the diluted compositions obtained by diluting the above compositions in water. Said diluted compositions comprise from 0.01% to 3.5% by weight of the total composition of said nonionic surfactant or said mixture of anionic surfactant and nonionic surfactant.

The present invention also encompasses a method of cleaning hard surfaces wherein a composition comprising at least one nonionic surfactant of the formula RO-(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>H wherein R is a  $C_8$  to  $C_{22}$  alkyl chain or a  $C_8$  to  $C_{28}$  alkyl benzene chain, and n is an integer of from 10 to 65, or mixtures thereof, is diluted in water and applied to said hard surface.

### Detailed description of the invention

The Compositions according to the invention comprise, as an essential ingredient, a highly ethoxylated nonionic surfactant. The highly ethoxylated nonionic surfactants to be used in the compositions according to the present invention are carefully selected, and belong to the group according to the formula  $RO-(CH_2CH_2O)_nH$ , wherein R is a  $C_8$  to  $C_{22}$  alkyl chain or a  $C_8$  to  $C_{28}$  alkyl benzene chain, and n is an integer

of from 10 to 65, or mixtures thereof. Indeed, it is unforeseeably only th se ethoxylated alcohols with such a high degree of thoxylation which allow to obtain the observed cleaning benefits in diluted form, especially on greasy soils. Accordingly, the preferred nonionic surfactants for use in the compositions according to the present invention are those according to the above formula where n is from 11 to 35, more preferably 18 to 35, most preferably 21 to 30. The preferred R chains for use herein are the Cg to C22 alkyl chains. Suitable chemical processes for preparing the highly ethoxylated nonionic surfactants for use herein have been extensively described in the art. Suitable highly ethoxylated nonionic surfactants for use herein are also commercially available, for instance in the series commercialized under the trade name LUTENSOL R from BASF or DOBANOL R from SHELL. A preferred highly ethoxylated alcohol for use herein is LUTENSOL R A030 (R is a mixture of C13 and C15 alkyl chains, and n is 30). It is also possible to use mixtures of such highly ethoxylated nonionic surfactants, with different R groups and different ethoxylation degrees.

The compositions according to the present invention may additionally comprise an anionic surfactant. The prior art extensively describes anionic surfactants, including alkyl benzene sulfates and sulfonates, paraffin sulfonates, sulfonates of fatty acids and of fatty acid esters, all of which are suitable for use herein. Said anionic surfactants can also be used in the form of their salts, including sodium, potassium, ammonium and triethanolammonium salts. The preferred anionic surfactants for use in the compositions according to the present invention are paraffin sulfonates, preferably in the form of their sodium salt.

When the compositions according to the present invention comprise both said highly ethoxylated nonionic surfactant and said anionic surfactant, these are preferably present in a weight ratio of said anionic surfactant to said nonionic surfactant of from 0.2 to 5, more preferably 0.5 to 2.5.

In one embodiment of the present invention, a hard surface cleaning composition according to the present invention comprises from 0.5 % to 30 %, preferably from 1 % to 15 % by weight of the total composition of

at least one nonionic surfactant of the formula RO- $(CH_2CH_2O)_nH$  wh rein R is a C<sub>8</sub> to C<sub>22</sub> alkyl chain r a C<sub>8</sub> to C<sub>28</sub> alkyl benzene chain, and n is an integer of from 21 to 65, or mixtures thereof.

In a second embodiment of the present invention, a hard surface cleaning composition according to the present invention comprises from 0.5 % to 30 %, preferably from 1 % to 15 % by weight of the total composition of a mixture comprising at least one anionic surfactant and at least one nonionic surfactant, wherein said nonionic surfactant is of the formula  $RO-(CH_2CH_2O)_nH$  wherein R is a  $C_8$  to  $C_{22}$  alkyl chain or a  $C_8$  to  $C_{28}$  alkyl benzene chain, and n is an integer of from 10 to 65, or mixtures thereof.

The diluted compositions according to the present invention, which are obtainable by diluting the compositions described hereinabove, comprise from 0.001 % to 3.5 % by weight of the total composition of the mixture described hereinabove, preferably from 0.01 % to 0.3 %.

The hard surface cleaning compositions according to the present invention may further comprise additional surfactants, including other nonionic surfactants, amphoteric and zwitterionic surfactants and mixtures thereof. Typical of these are lower ethoxylated nonionic surfactants (e.g with an ethoxylation degree of about 7), amine oxides, betaines, sulphobetaines and the like, which are well-known in the detergency art.

The compositions according to the present invention may further comprise an alkanolamine, or mixtures thereof, in amounts ranging from 0.1% to 10 % by weight of the total composition, preferably from 0.5% to 5%, most preferably from 0.8% to 3%. At such levels, the alkanolamine has a buffering effect in the undiluted product, as well as an unexpected boosting effect on the cleaning performance of the diluted compositions. Suitable alkanolamines for use in the compositions according to the present include monoalkanolamines, dialkanolamines, trialkanolamines, alkylalkanolamines, dialkylalkanolamines and alkoxyalkanolamines. Preferred alkanolamines to be used according to the present invention include monoethanolamine, triethanolamine, aminoethylpropanediol, 2-

6

aminomethyl propanol, and ethoxyethanolamine. Particularly preferred are m noethanolamine, triethanolamine and ethoxyethanolamine.

The compositions according to the present invention may further comprise builders. Suitable builders for use herein include nitrilotriacetates (NTA), polycarboxylates, citrates, water-soluble phosphates such as tripolyphosphate and sodium ortho-and pyro-phosphates, silicates, ethylene diamine tetraacetate (EDTA), amino-polyphosphonates (DEQUEST), ether carboxylate builders such as in EP-A-286 167, phosphates, iminodiacetic acid derivatives such as described in EP-A-317 542, EP-262 112 and EP-A-399 133, and mixtures thereof. Preferred builders/sequestrants for use herein are selected from Tetrapotassium pyrophosphate, citric acid and sodium carbonate. The hard surface cleaning compositions according to the present invention may comprise up to 15% by weight of the total composition of a builder, preferably from 1% to 10%

The compositions according to the present invention may further comprise solvents. Suitable solvents for use herein include propylene glycol derivatives such as n-butoxypropanol or n- butoxypropoxypropanol, watersoluble CARBITOL R solvents or water-soluble CELLOSOLVE R solvents: water-soluble CARBITOL R solvents are compounds of the 2-(2alkoxyethoxy)ethanol class wherein the alkoxy group is derived from ethyl, propyl or butyl; a preferred water-soluble carbitol is 2-(2butoxyethoxy)ethanol also known as butyl carbitol. Water-soluble CELLOSOLVE R solvents are compounds of the 2-alkoxyethoxy ethanol class. with 2-butoxyethoxyethanol being preferred. Other suitable solvents include benzyl alcohol, and diols such as 2-ethyl-1, 3-hexanediol and 2,2,4-trimethyl-1,3-pentanediol and mixtures thereof. Preferred solvents for use herein are n-butoxypropoxypropanol, BUTYL CARBITOL R and mixtures thereof. The compositions according to the present invention comprise up to 15 % by weight of the total composition of a solvent, preferably from 3% to 10%.

The compositions according to the present invention may also comprise minor ingredients to provide aesthetic or additional product performance benefits. Typical minor ingredients include perfumes, dyes, optical brighteners, soil suspending agents, detersive enzymes, gel-control

agents, thickeners, freeze-thaw stabilizers, bactericides, preservatives, and the like.

In the method for the cleaning of hard surfaces according to the present invention, a hard surface cleaning composition comprising at least one nonionic surfactant of the formula RO-(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>H wherein R is a C<sub>8</sub> to C<sub>22</sub> alkyl chain or a C<sub>8</sub> to C<sub>28</sub> alkyl benzene chain, and n is an integer of from 10 to 65, or mixtures thereof, is diluted in water and applied to said hard surface. In a preferred method according to the present invention, said composition further comprises an anionic surfactant as described hereinbefore.

In a preferred method according to the present invention, said composition is diluted into 10 to 200 times its weight of water, more preferably 50 to 150 times, before it is applied to said hard surface.

The different embodiments of the present invention are further illustrated by the following examples

#### Examples

The following compositions were made by mixing the listed ingredients in the listed proportions:

	Co	ompositi	lons	,	
	#1	#2	#3	#4	
Ingredients:		Weigh	nt %		
Sodium paraffin sulfonate	. 3	3	3	3	
Alcohol ethoxylate 30E0 (1)	2	-	-	2	
Alcohol ethoxylate 12EO (2)	•	3	•	-	
Alcohol ethoxylate 7EO (3)	1	-	-	1	
Alcohol benzene ethoxylate 10E0 (4)	-	•	3	-	
Citric acid	2	2	2	3	
Butylcarbitol R	4	. 4	4	7	
n-butoxypropoxypropanol	-	-	-	2.5	
Triethanolamine	1	1	2	1	
water & minors		up to	100%		

	C	Compositions		
	#5	#6	#7	#8
Ingredients:		Weigh	t %	
Sodium paraffin sulfonate	. 3	-	-	-
Sodium alkyl sulfate	· -	3	-	-
Sodium alcohol ethoxylate sulfate	•	• •	3	•
Alcohol ethoxylate 30EO (1)	2	2	-	4
Alcohol ethoxylate 12EO (2)	1	, -	3	-
Alcohol ethoxylate 7EO (3)	-	1	-	•
Citric acid	4	3	4	-
Tetrapotassium pyrophosphate		-	-	4
Butylcarbitol R	.4	4	6	5
n-butoxypropoxypropanol		÷ .	··· ·> = ·>	2
Triethanolamine	-	1.	2	-
Monoethanolamine	2		· -	-
Ethoxyethanolamine	-	<b>-</b> ,		2
water & minors		up to	100%	

In the examples hereinabove, (1) is a highly ethoxylated nonionic surfactant wherein R is a mixture of  $C_{13}$  and  $C_{15}$  alkyl chains and n is 30. (2) is a highly ethoxylated nonionic surfactant wherein R is a mixture of  $C_{13}$  and  $C_{15}$  alkyl chains and n is 12. (3) is a lower ethoxylated nonionic surfactant wherein n is 7. (4) is a highly ethoxylated nonionic surfactant wherein R is a mixture of  $C_{19}$  and  $C_{21}$  alkyl benzene chains and n is 10.

Compositions 1-8 described hereinabove can be used neat or diluted. In a method according to the present invention, these compositions are diluted in 65 times their weight of water and applied to a hard surface.

#### What is claimed is:

- 1. A hard surface cleaning composition comprising from 0.5 % to 30 % by weight of the total composition of at least one nonionic surfactant, characterized in that said nonionic surfactant is of the formula RO-(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>H wherein R is a C<sub>8</sub> to C<sub>22</sub> alkyl chain or a C<sub>8</sub> to C<sub>28</sub> alkyl benzene chain, and n is an integer of from 21 to 65, or mixtures thereof.
- 2. A hard surface cleaning composition comprising from 0.5 % to 30 % by weight of the total composition of a mixture comprising at least one anionic surfactant and at least one nonionic surfactant, characterized in that said nonionic surfactant is of the formula RO-  $(CH_2CH_2O)_nH$  wherein R is a  $C_8$  to  $C_{22}$  alkyl chain or a  $C_8$  to  $C_{28}$  alkyl benzene chain, and n is an integer of from 10 to 65, or mixtures thereof.
- 3. A composition according to claim 2 wherein said anionic surfactant and said nonionic surfactant are present in a weight ratio of said anionic surfactant to said-nonionic surfactant of from 0.2 to 5, preferably 0.5 to 2.5.
- 4. A composition according to claims 2 and 3, wherein said anionic surfactant is a paraffin sulfonate in the form of its sodium salt.
- 5. A composition according to claims 2 to 4 wherein n is an integer of from 11 to 35, preferably 18 to 35.
- A composition according to any of the preceding claims wherein n is an integer of from 21 to 30.
- 7. A composition according to any of the preceding claims, wherein R is a  $C_8$  to  $C_{22}$  alkyl chain.

....

一个人的

- 8. A diluted hard surface cleaning composition obtainable by diluting in water a composition according to any of the preceding claims, comprising from 0.001 % to 3.5 %, preferably from 0.01 % to 0.3 % by weight of the total composition of said nonionic surfactant or said mixture of anionic surfactant and nonionic surfactant.
- 9 .A method for the cleaning of a hard surface wherein a composition comprising at least one nonionic surfactant of the formula RO-(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>H wherein R is a C<sub>8</sub> to C<sub>22</sub> alkyl chain or a C<sub>8</sub> to C<sub>28</sub> alkyl benzene chain, and n is an integer of from 10 to 65, or mixtures thereof, is diluted in water and applied to said hard surface.
- 10.A method according to claim 9 wherein said composition further comprises an anionic surfactant.

3. 494

11.. A method according to claims 9 and 10, wherein said composition is diluted into 10 to 200 times its weight of water, more preferably 50 to 150 times, before it is applied to said hard surface.

## INTERNATIONAL SEARCH REPORT

International application No. PCT/US93/02335

	<u>:</u>		Ar to make the con-
	SSIFICATION OF SUBJECT MATTER :C11D 1/722, 1/83		
	:252/174.21,170,171,550,551,554, DIG. 10, DIG. 10 International Patent Classification (IPC) or to both		·
B. FIEL	DS SEARCHED		
Minimum d	ocumentation searched (classification system followed	by classification symbols)	
U.S. ;			
Documentat	ion searched other than minimum documentation to the	extent that such documents are included	in the fields searched
Electronic d	ata base consulted during the international search (na	me of data base and, where practicable,	search terms used)
C. DOC	UMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where ap	propriate, of the relevant passages	Relevant to claim No.
X	US,A, 4,492,646 (WELCH) 08 JANUARY 1985		1-3,9 & 10
	See abstract; column 2, lines 30-52 an	d examples VI	
X	US,A, 4,615,819 (LENG ET AL) 07 OCTOBER 1986		2,3,9 and 10
	See abstract and example 18		
X	US,A, 4,671,894 (LAMB ET AL) 09 JUNE 1987		2,3,9 and 10
	See abstract and example i		
	٠ ,	• .	
	·		
Furth	ner documents are listed in the continuation of Box C	. See patent family annex.	
• Sp	ecial categories of cited documents:	"T" inter document published after the inte date and not in conflict with the applic	mational filing data or priority
to	cument defining the general state of the art which is not considered be part of particular relevance	principle or theory underlying the inv	estica
·L· do	riier document published on or after the international filing date cument which may throw doubts on priority claim(a) or which is ed to establish the publication date of another citation or other	"X" document of particular relevance; the considered novel or cannot be conside when the document in taken alone	red to involve an inventive step
"O" qo	ecial reason (as specified)  cument referring to an oral disclosure, use, exhibition or other	"Y" document of particular relevance; the considered to involve an inventive combined with one or more other suc	step when the document is a documents, such combination
·P· do	came cument published prior to the international filing date but later than e priority date claimed	being obvious to a person skilled in it "&" document member of the same patent	
Date of the 26 APRIL	actual completion of the international search . 1993	Date of mailing of 99 crnational see	rch report
	nailing address of the ISA/US	Authorized officer Ngorth	Nquyen
Box PCT	n, D.C. 20231	BRADLEY A. SWOPENGULEN	NGOC-IIO
i _	io. NOT APPLICABLE	Telephone No. (703) 308-2521	Tickal division

Form PCT/ISA/210 (second sheet)(July 1992)\*

## INTERNATIONAL SEARCH REPORT

International application No. PCT/US93/02335

Box I	Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)
This inte	ernational report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:
1.	Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:
	·
2.	Claims Nos.:
ب	because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
_	
3. <u>x</u>	Claims Nos.: 4-8 and 11 because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).
Box II	Observations where unity of invention is lacking (Continuation of item 2 of first sheet)
This Inte	ernational Searching Authority found multiple inventions in this international application, as follows:
។ មិនស៊ីប	
4	
ı. 🗀	As all required additional search fees were timely paid by the applicant, this international search report covers all search
ــا	claims.
2.	As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite paym of any additional fee.
3.	As only some of the required additional search fees were timely paid by the applicant, this international search report cov only those claims for which fees were paid, specifically claims Nos.:
	only those claims for which fees were paid, specifically claims Nos.:
4.	No required additional search fees were timely paid by the applicant. Consequently, this international search report restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
	•.
Remark	k on Protest The additional search fees were accompanied by the applicant's protest.
	No protest accompanied the payment of additional search fees.